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Energy upgrading by solid–gas reaction heat transformer: A critical review

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Abstract

The solid–gas reaction heat transformer, which can upgrade the temperature of middle-grade heat (such as industrial waste heat, solar energy, geothermal energy, etc.) is considered promising for energy-saving in the near future. It provides high storage capacity of heat, wide range of working temperatures as compared to other heat transformers. In addition, it uses all natural working pairs, which are friendly to the environment. For its complicated chemical kinetics, high requirement for safety, low system efficiency, large investment, etc., it has not been widely used yet. This paper gives a comprehensive review of the research done on solid–gas reaction heat transformers regarding the status of technology (such as thermodynamic cycles, working pairs, system performance, etc.) and current applications and future prospect, with special reference to effective utilization and storage of industrial waste heat and solar energy, long-distance heat transport and district heat supply, etc.

Keywords: Solid–gas reaction heat transformer; Working pairs; Thermodynamic cycles; System performance; Application

Contents

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1. Introduction

Energy problem has attracted people's attention since the worldwide energy crisis happened in 1970s. Energy is indispensable in our modern society, but unfortunately the reserve of fossil energy resources, such as coal, oil and natural gas, are gradually exhausting. On the other hand, there is a lot of middle-grade heat from renewable energy (e.g. solar energy, geothermal energy etc.) or waste heat (e.g. heat discharged from industrial factories, electric power plants, etc.) left unused due to their relatively low grade. If the temperature can be upgraded, they will be useful again in many fields. Thus, developing a technology to lift the temperature of middle-grade heat would contribute greatly to energy-saving.

Usually, the economical methods to get temperature lift include electrical means (vapor compression heat pump), and thermal means (absorption, adsorption and chemical reaction heat transformers). Although the electrical heat pump has higher system efficiency than the heat transformer, it still consumes high-grade electric energy. Heat transformers, which are directly driven by the middle-grade renewable energy or waste heat, have attracted many researchers' interest all over the world [1–3]. With the deepening of the research, people have found that the advantages of solid–gas reactions, such as high storage capacity of heat, wide range of working temperatures, long storage term of both reactants and products, low heat loss, etc., suggest that it could be an optimal option for upgrading the temperature of middle-grade heat as well as energy storage. So solid–gas reaction heat transformers have been developed rapidly since 1990s [3–6].

Various chemical substances can be used in the solid–gas heat transformers, and Table 1 gives some main working pairs according to different reactive gas. There are ammonia system (alkaline salts/ammonia, alkaline earth salts or metallic halides/ammonia, nitrates or phosphates/ammonia, monomethylamine/ammonia), sulfur dioxide system (oxides/sulfur dioxide), water vapor system (oxide/water vapor, salts/water vapor), carbon dioxide system (oxides/carbon dioxide), hydrogen system (metals or metal alloys/hydrogen), etc. The mostly used working pairs are chloride/ammonia and metal hydride/hydrogen, whose ozone depletion potential (ODP) and global warming potential (GWP) are all zero [7].

This paper presents a review of the work done on solid–gas heat transformers in the past decades. With different arrangements of working pairs, there exist two kinds of

Nomenclature

C	heat capacity ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
COP	coefficient of performance
$\mathrm{COP_{ex}}$	exergy efficiency
e_x	exergy (J)
G	reactive gas
ΔH	enthalpy change ($\mathrm{J\,mol^{-1}}$)
n	mole ratio of reactive gas to solid salt
P	pressure (Pa)
Q	heat (J)
R	mole gas constant
S	reactive salt
S'	produced compound
ΔS	entropy change ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
T	temperature (K if not specified)
$\mathrm{d}T_1$	temperature difference for supercooling, superheat and heat transfer (K)
$\mathrm{d}T_2$	temperature difference for solid–gas reaction (K)
ΔT	temperature lift (K)
W	reactive mole (mol)
ϕ	heat exchange efficiency

Subscripts

c	condensation
d	decomposition
e	evaporation
eq	equilibrium
G	gas
h	high
in	input
l	low
m	middle
r	reaction
s	synthesis
S	reactive salt

thermodynamic cycles for single-stage heat transformers and five kinds of cycles for two-stage ones. The working pairs of chlorides/ammonia and metal hydrides/hydrogen are mainly discussed and others are also introduced. Besides, a thermal–chemical method using Clapeyron diagram is described to help select appropriate working pairs of chlorides for different types of heat transformers. Some parameters as coefficient of performance (COP) and temperature lift are derived and used for the comparison of thermodynamic cycles. Various models and related simulation results are presented to study system performance both statically and dynamically. These results are useful to guide the

Table 1
Classification of solid–gas thermo-chemical systems

Ammonia system	Sulfur dioxide system	Water vapor system	Carbon dioxide system	Hydrogen system
Alkaline salts (e.g. NaOH)/NH_3 Alkaline earth salts (e.g. $CaCl_2$); metallic halides (e.g. $MnCl_2$, $NiCl_2$)/NH_3 Nitrates, phosphates/NH_3 Monomethylamine/NH_3	Oxides (e.g. CaO)/SO_2	Oxides (e.g. MgO, CaO, Na_2O)/H_2O Salts (e.g. $CaCl_2$, Na_2S)/H_2O	Oxides (e.g. CaO, BaO, PbO)/CO_2	Metals (e.g. Ca, Ni, Mn, Al)/H_2 Metal alloys (e.g. $LaNi_5$)/H_2

construction or optimization of practical systems in the near future. In the last part of the paper, some existing theoretical and practical problems have been proposed for further research.

2. Research status

Although the basic thermodynamic cycle has been known since the beginning of the last century, intensive research and development, as well as applications, had not begun to develop until a decade ago [4]. So far, most research is focused on thermodynamic cycles, selection of working pairs, system performance, etc., to make preparation for the realization of various functional heat transformer systems.

2.1. Thermodynamic cycles

The general reaction taking place in the reactor is of the form

$$S + nG \leftrightarrow S' + n\Delta H_{\mathrm{r}}, \tag{1}$$

where the synthesis and decomposition reactions occur at two different temperatures corresponding to different pressures. It is noted that solid–gas reaction equilibrium and the liquid–vapor equilibrium are both mono-variant systems, which can be described by the Van't Hoff expression:

$$\ln(P) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}. \tag{2}$$

In Clapeyron diagram, they are expressed as two straight lines. The thermodynamic cycles of heat transformers can be fixed in Clapeyron diagram if the certain working pairs and working conditions (e.g. pressure or temperature) are known.

2.1.1. Cycles of single-stage solid– gas heat transformers

The simplest way to achieve temperature lift is the basic thermodynamic cycle [5], which consists of a reactor, where the solid–gas synthesis or decomposition reaction happens, and a heat exchanger, where the evaporation or condensation of the gas takes place, as shown in Fig. 1. The cycle is described by a liquid/vapor equilibrium line (L/V line) and a solid/gas reaction equilibrium line (S/G line) in Clapeyron's

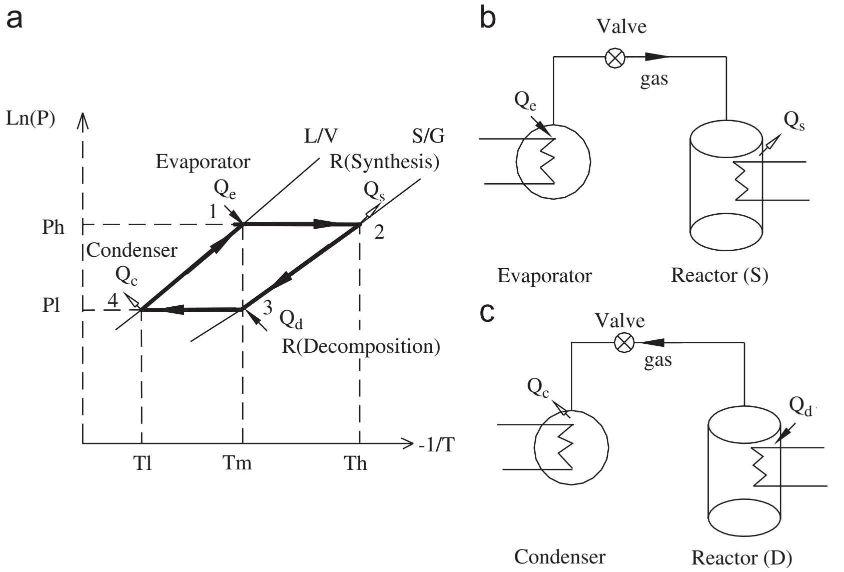


Fig. 1. Clapeyron's diagram showing operation mode of basic single-stage heat transformer [5].

diagram in Fig. 1(a). First, in the generating period, the middle-grade heat at T_m is supplied to the heat exchanger (acting as an evaporator) so the liquid in it evaporates; the pressure of evaporator rises to P_h (point 1) and the valve is opened; the high pressure gas enters the reactor to synthesize with the reactive salt, releasing high-grade heat Q_s at T_h (point 2); the evaporation and the synthesis reaction continues so the pressure P_h remains steady; when the synthesis reaction in the reactor finishes, the valve is closed, as shown in Fig. 1(b). Immediately, the reactor is supposed to be cooled. Then in the recovering period, the middle-grade heat at T_m, which may be different from the former, is supplied to the reactor for decomposition; once the pressure of reactor rises to P_l (point 3), the valve is opened; the released gas transfers to the heat exchanger (acting as a condenser) to be condensed by the coolant, releasing condensation heat Q_c at T_l (point 4); when the decomposition reaction finishes, the valve is closed, as shown in Fig. 1(c). Then the condenser is supposed to be heated before the next cycle, and the cycle continues. Obviously, more than two heat exchangers and two reactors are required to realize continuous cycle so as to get continuous useful high-grade heat output. Unfortunately such reactor–heat exchanger configuration is not very suitable for ammonia and hydrogen systems, for their high system pressure will cause the safety problem because of the coexistence of vapor and liquid in the same heat exchanger.

To overcome this shortcoming, the two-salt cycle has been proposed by Spinner et al. in 1993 [5], as shown in Fig. 2. In Clapeyron's diagram, an S/G line has replaced the L/V line on the left side, as shown in Fig. 2(a); and the configuration of system comprises of two reactors with different reactive solid salts, shown in Fig. 2(b). The working principle is more or less the same as the above one; only the condensation and evaporation in the heat exchanger are replaced by synthesis and decomposition reactions.

2.1.2. Cycles of two-stage and multi-stage solid–gas heat transformers

The limited temperature lift and system efficiency for single-stage heat transformers can be overcome by two-stage or multi-salt systems.

Suda et al. introduced the two-stage three-salt cycle using three different kinds of metal hydrides [8], as shown in Fig. 3. It is made up of three reactors which work under three different pressures. During the operation, the synthesis or decomposition reaction occurs

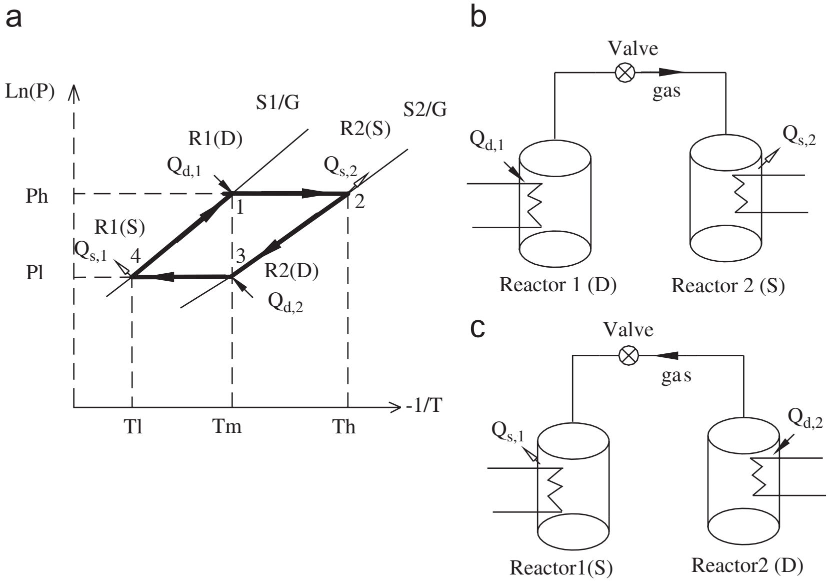


Fig. 2. Clapeyron's diagram showing operation mode of single-stage two-salt heat transformer [5].

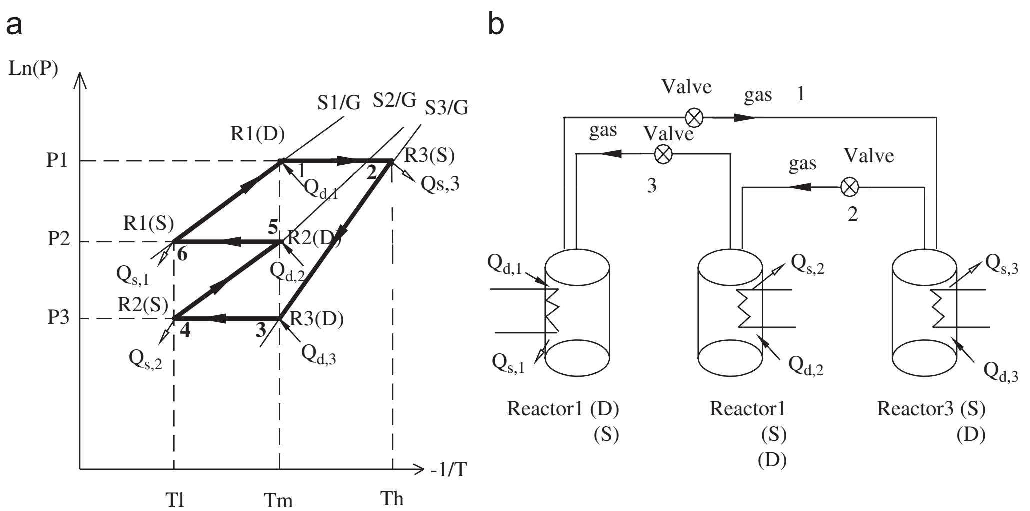


Fig. 3. Clapeyron's diagram showing operation mode of two-stage three-salt heat transformer [8].

between any two reactive salts. It can be divided into one generating period (point 1 to point 2 in Fig. 3(a)) and two recovering periods (point 3 to point 4 and point 5 to point 6) as well as cooling or heating period after each.

Sun has proposed another possible three-salt cycle [9] to increase system efficiency, as shown in Fig. 4. Though it is also made up of three reactors, it has two generating periods (point 1 to point 2 and point 3 to point 4 in Fig. 4(a)) and one recovering period (point 5 to point 6). So we call it double-effect three-salt cycle. Its COP would be two times of the above one, but the temperature lift decreases a lot.

The internal heat exchange between different reactors, using the synthesis heat produced by one reactant for another's decomposition, is necessary to reduce the amount of heat input, and consequently to obtain a satisfactory COP. The combination of L/V and S/G lines has enabled to define a certain number of systems, such as the two-salt system with internal heat exchange [10], the three-salt system with internal heat exchange [6], the four-salt system with internal heat exchange [11], etc.

The two-salt system with internal heat exchange is made up of two reactors and two heat exchangers, as shown in Fig. 5. Each reactor is connected with a heat exchanger, so the system can be taken as two basic single-stage ones which operate under the same pressure range but different temperature ranges and are connected by an internal heat exchange process (point 2 to point 4 in Fig. 5(a)). There are two generating periods (point 1 to point 2 and point 1 to point 3) and two recovering periods (point 4 to point 6 and point 5 to point 6).

Replacing the L/V line with an S/G line in the above cycle, we get a new type of three-salt system with internal heat exchange, as shown in Fig. 6. It consists of four reactors. The working principle is more or less the same. Comparing with the above cycle, it can effectively reduce the system pressure while achieving the same temperature lift or it can get higher temperature lift under the same pressure range.

Then a new four-salt system with internal heat exchange has been proposed, as shown in Fig. 7. It is made up of four reactors, which can be taken as two single-stage two-salt systems that work under different temperature and pressure ranges and are connected by

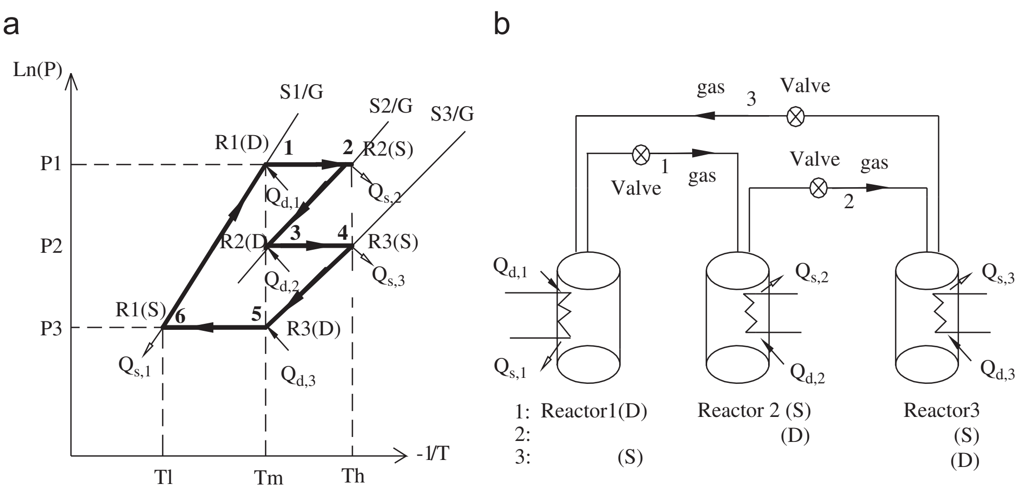


Fig. 4. Clapeyron's diagram showing operation mode of two-stage double-effect three-salt heat transformer [9].

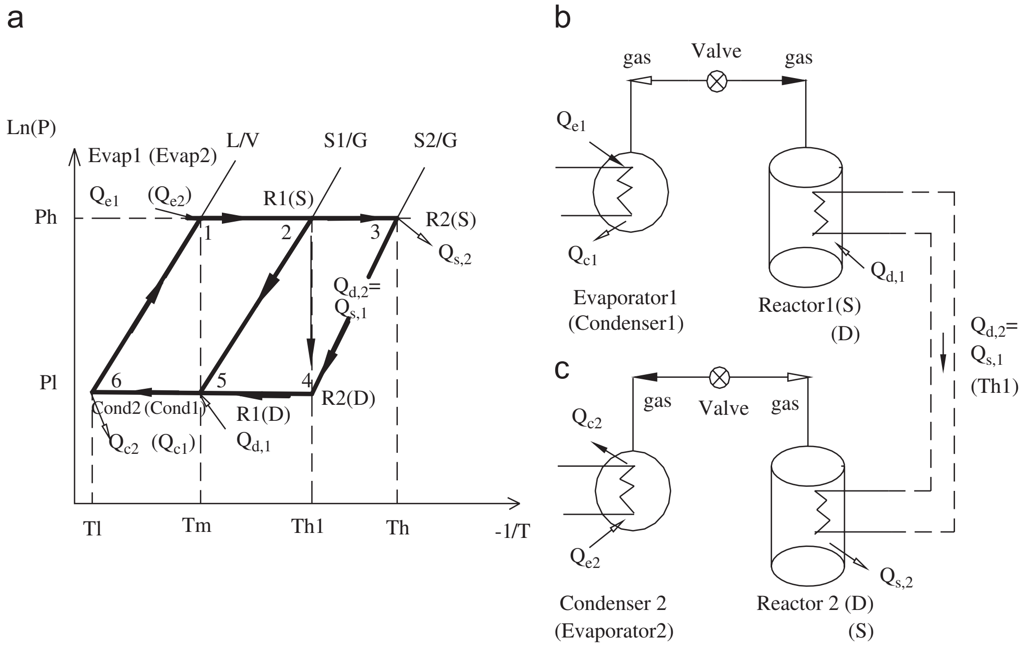


Fig. 5. Clapeyron's diagram showing operation mode of two-stage two-salt heat transformer with internal heat exchange [10].

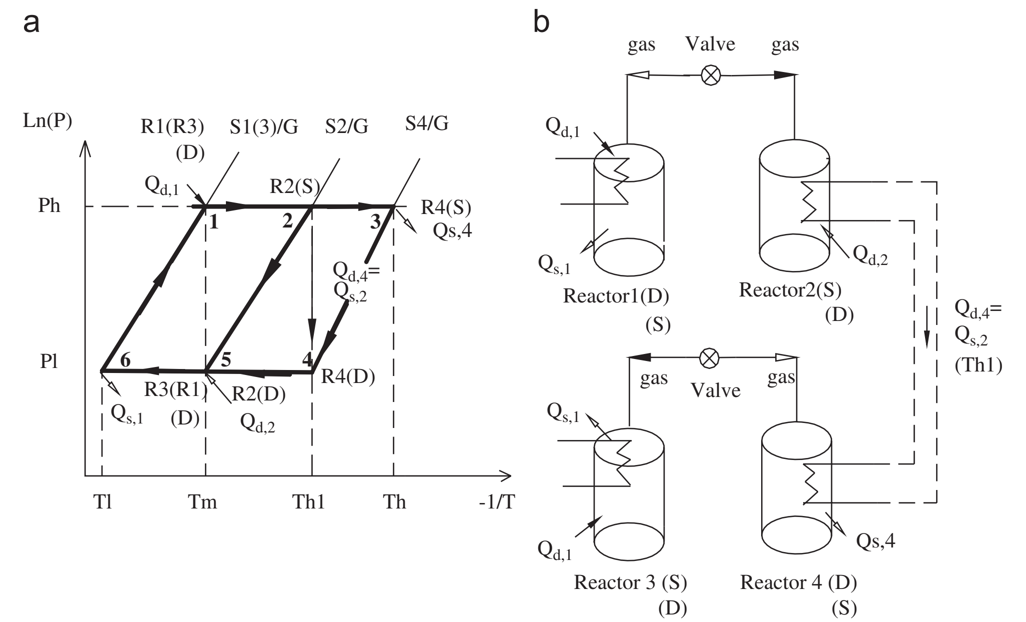


Fig. 6. Clapeyron's diagram showing operation mode of two-stage three-salt heat transformer with internal heat exchange [6].

the internal heat exchange process (point 2 to point 3 in Fig. 7(a)). The low-temperature part is made up of reactors 1 and 3, whose working pressure is between P_2 and P_3; while the high-temperature part is made up of reactors 2 and 4, whose working pressure is between P_1 and P_4. There are two generating periods (point 1 to point 2 and point 3 to point 4) and two recovering periods (point 5 to point 6 and point 7 to point 8).

The multi-salt cycle has been proposed [12] for a higher efficiency from the heat wave concept. It implements a L/V line and several S/G lines (e.g. six S/G lines as shown in Fig. 8). In each reactor, there are several reactive salts instead of one placed in the increasing order of their equilibrium temperatures under certain pressure, so in synthesis or decomposition process, heat wave will be formed in the flowing direction of the hot fluid. The advantage of this method is that it improves the system efficiency through increasing thermal potential in reactors.

2.1.3. Actual cycles of heat transformers

Actual cycles are more complicated than ideal ones given different mole ratios of reactive gas to solid salt in chemical reactions, various sensible-heat exchanges, and unbalanced temperature differences. The unbalanced temperature differences, such as supercooling, superheating and temperature difference for heat transfer and solid–gas reaction are necessary for actual cycles to ensure the well going of solid–gas reactions [10]. Take the two-stage heat transformer shown in Fig. 7 as an example, the state point is not right on the equilibrium line in Clapeyron's diagram any more, as shown in Fig. 9. Due to the sensible-heat exchanges, the heating processes of reactor 1 and reactor 2 from low-temperature T_l to middle-temperature T_m will increase heat input, and heating reactor 4 from T_m to T_h will decrease high-grade heat output; while the cooling process of reactor 4

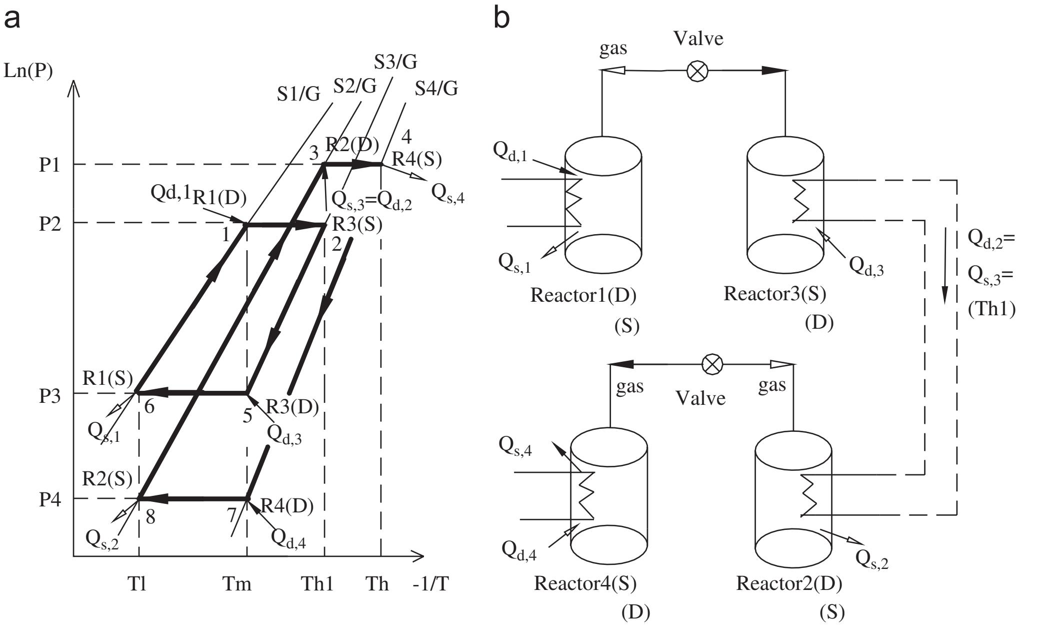


Fig. 7. Clapeyron's diagram showing operation mode of two-stage four-salt heat transformer with internal heat exchange [11].

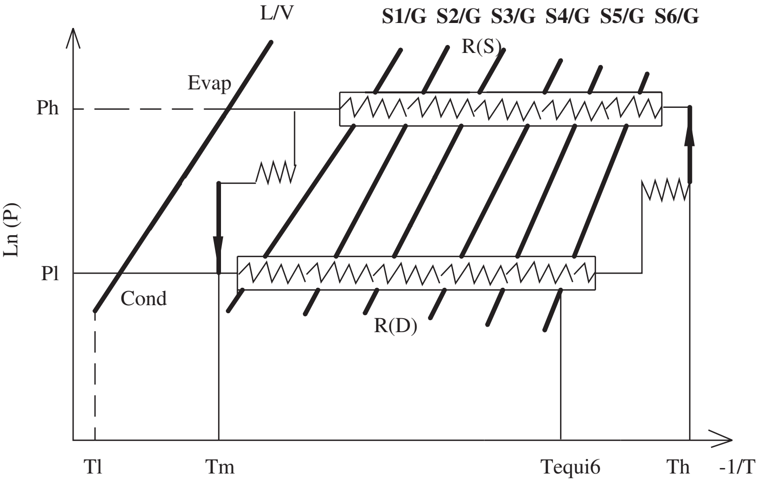


Fig. 8. Clapeyron's diagram showing operation mode of multi-stage heat transformer [12].

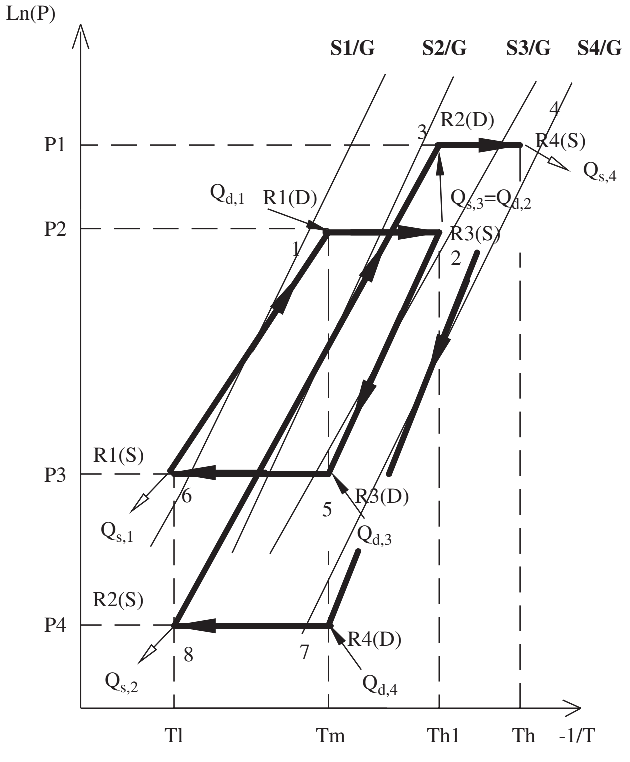


Fig. 9. Clapeyron's diagram showing actual cycle of two-stage four-salt heat transformer with internal heat exchange.

from T_h to T_m will decrease heat input. Besides, the internal heat exchange between reactor 2 and reactor 3 will also decrease heat input and thus improve system efficiency.

2.2. Working pairs

Solid–gas working pairs play an important role because thermal energy is stored and released by thermo-chemical reactions. So at the very beginning, a large number of solid–gas reactions and the methods to select proper working pairs have been studied. The major requirements for working pairs include large heat storage capacity, good thermal conductivity, high specific power output, fine thermal stability under working conditions (certain temperature and pressure ranges), well transportability (easy to handle), small specific volume, non-corrosive and non-toxic (environmental friendly), etc. [13]. Besides, ideal working pairs should also meet matching requirements for reaction temperature and rate, so as to improve system efficiency, to reduce equipment size and to shorten cycling time, etc. [14].

2.2.1. Various working pairs

A lot of solid salts (alkaline, alkaline earth or metallic halides, nitrates, phosphates, sulphates, monomethylamine, etc.) can react with ammonia. Touzain [15] has examined about 350 kinds of solid salts/ammonia reactions in 70 references of the last century and given out their thermodynamic values like entropy, enthalpy, etc. However, Goetz et al. [5] have pointed out that the probable reactants to be used will be among the chlorides of Ca, Mn, Mg, Fe, Ni, Ba, Sr and have made a concise summary of chloride working pairs for single-stage two-salt heat transformer. Chen and Tan [16] got the similar conclusion from experiments. Fig. 10 shows reaction equilibrium lines for 36 kinds of chloride ammoniates [10]. Their reaction heats are of the same order of magnitude, typically $\Delta H_r = 50 \pm 15\,\mathrm{kJ\,mol^{-1}}$, so the equilibrium lines of those chlorides in the Clapeyron diagram will thus be virtually parallel or will only cross at very high pressure. The special case in ammonia system is that a reactive salt's S/G line (e.g. a sulphate's), will sometimes cross that of a chloride in the Clapeyron diagram [5], as shown in Fig. 11, and this leads to the definition of the so called "double-effect heat transformer". There are two temperature levels of produced heat T_h and T_{h1} and two heat sources at T_l and T_m are required. Its ideal COP can be much higher for it uses low-grade heat (e.g. heat from the ambient air) as part of heat input, which is not taken into account in the calculation of the COP. The same is true for some metal hydrides. But in fact, the number of working pairs whose S/G lines are crossed is found to be limited until now. So if such "double-effect heat transformer" will be used in practice, more efforts are needed to find suitable reactive salts.

To overcome the high pressure problem in ammonia system, some researchers have recommended using methanol gas instead of ammonia to react with chlorides [17]. The methanol has low freezing temperature of $-98\,^{\circ}\mathrm{C}$, high condensation temperature of $64.7\,^{\circ}\mathrm{C}$ and large latent heat of vaporization of $1178\,\mathrm{KJ\,kg^{-1}}$ [18]. The chloride/methanol heat transformer is considered one of the most promising systems and now many researchers are engaged in studying it. Balat and Spinner [19] have done experiments on $CaCl_2/CH_3NH_2$ system, and obtained better system performance.

Metal hydride is a new kind of functional material developed in recent 20 years. It can react with a large amount of hydrogen with obvious heat effects. Hydrogen's condensation temperature is so low that the conventional heat exchanger–reactor configuration cannot

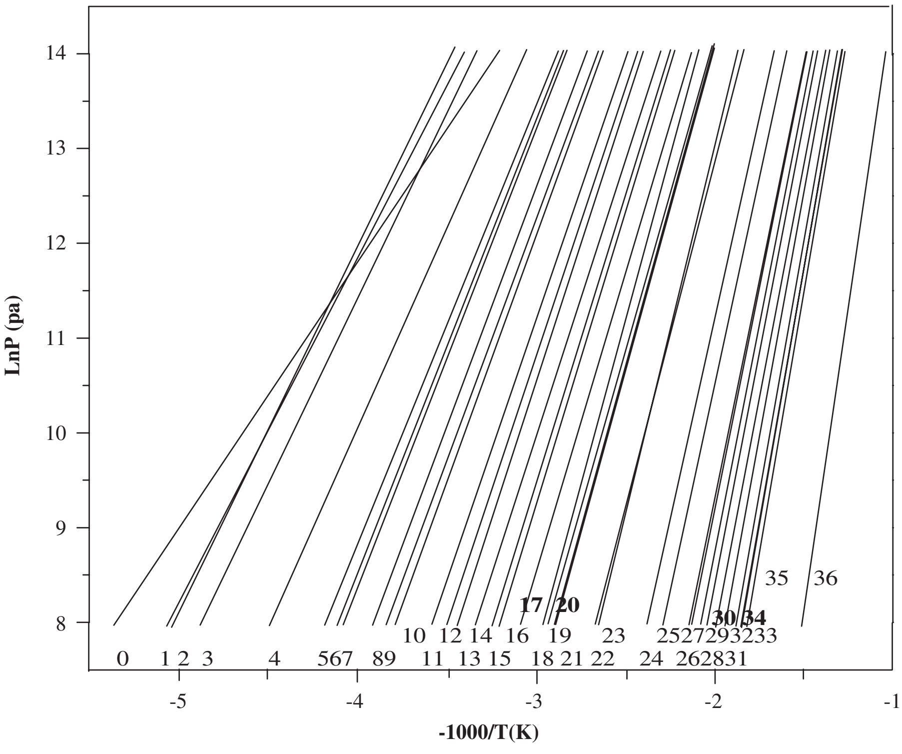


Fig. 10. Equilibrium lines for 36 kinds of chloride ammoniates [10]. 0:NH_3, 1:$ZnCl_2$(10/6), 2:$CuCl_2$(10/6), 3:$SnCl_2$(9/4), 4:$PbCl_2$(8/3.25), 5:$BaCl_2$(8/0), 6:$SnCl_2$(4/2.5), 7:$PbCl_2$(3.25-2), 8:$CaCl_2$(8/4), 9:$SrCl_2$(8/1), 10:$CaCl_2$(4/2), 11:$ZnCl_2$(6-4), 12:$PbCl_2$(2/1.5), 13:$PbCl_2$(1.5/1), 14:$MnCl_2$(6/2), 15:$ZnCl_2$(4/2), 16:$CuCl_2$(5/3.3), 17:$FeCl_2$(6/2), 18:$CuCl_2$(3.3/2), 19:$CoCl_2$(6/2), 20:$PbCl_2$(1/0), 21:$MgCl_2$(6/2), 22:$NiCl_2$(6/2), 23:$CaCl_2$(2/1), 24:$CaCl_2$(1/0), 25:$MnCl_2$(2/1), 26:$MgCl_2$(2/1), 27:$FeCl_2$(2/1), 28:$CoCl_2$(2/1), 29:$NiCl_2$(2/1), 30:$ZnCl_2$(2/1), 31:$MnCl_2$(1/0), 32:$FeCl_2$(1/0), 33:$MgCl_2$(1/0), 34:$CoCl_2$(1/0), 35:$NiCl_2$(1/0), 36:$ZnCl_2$(1/0). *Note:* the $ZnCl_2$(10/6) line stands for the equilibrium line of reaction $ZnCl_2{\cdot}6NH_3 + 4NH_3 \leftrightarrow ZnCl_2{\cdot}10NH_3$ and the same as followings.

be realized. There are usually two reactive beds connecting with heat and cold sources in turn in a metal hydride/hydrogen heat transformer, and the hydrogen is cycled so as to achieve temperature lift [20]. Huston and Sandrock [21] have summarized properties of different metal hydrides for our reference, i.e. pressure–temperature relationship, hysteresis, hydrogen capacity, heat capacity, etc. The normal metal hydrides used are AB_5, AB, A_2B type alloys with the major compounds of La, Lm or Ni, or with part of the Ni replaced by Al, Mn, Cu, Fe, etc., such as $LmNi_{4.85}Sn_{0.15}$, $LmNi_{4.49}Co_{0.1}Mn_{0.205}Al_{0.205}$, $LaLmNi_{4.4}Co_{0.2}Mn_{0.2}Al_{0.2}$, etc., as shown in Fig. 12. Their temperature lift varies from 16 to 110 °C [22].

Comparatively, reaction heat of oxide/water vapor or oxide/carbon dioxide is larger and the reacting temperature is higher, so the corresponding system could realize larger heat output and higher temperature lift. For example, heat transformer using working pairs of MgO/H_2O and being driven by middle-grade heat of 100 °C could export heat of 170 °C; and the system with working pairs of CaO/CO_2 and PbO/CO_2 can lift heat from 100 to 700 °C and 880 °C, respectively [23]. de Boer et al. [24] investigated the thermodynamic

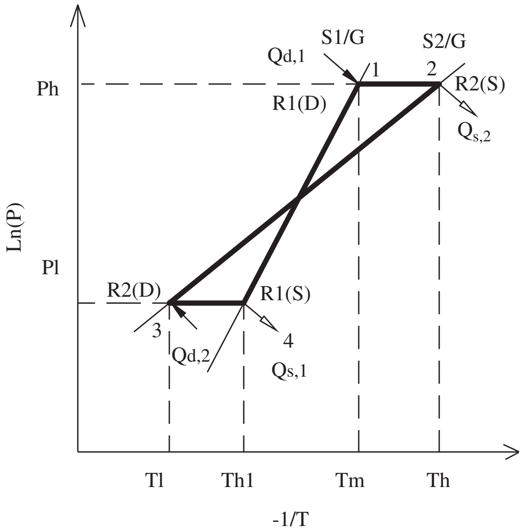


Fig. 11. Clapeyron's diagram showing operation mode of single-stage double-effect two-salt heat transformer [5].

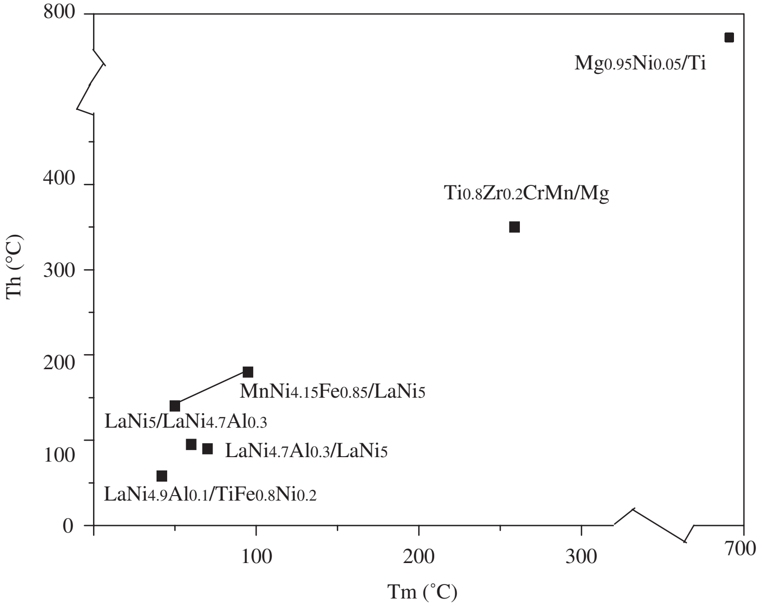


Fig. 12. Common metal hydride pairs and corresponding temperature lifts (data from [22]).

characteristics of Na_2S/H_2O reacting system and derived their vapor pressure–temperature equilibrium line and a set of thermodynamic relations to make preparation for use in heat transformers.

Rockenfeller and Kirol [25] have explored the application potential of complex compounds like compounds of ammoniates and metal hydrides which can reversibly bond

and release water vapor or ammonia. These compounds promise the power densities of 5–10 times that of traditional salts with the cycling time of 5–12 min. Currently, some new consolidated materials made of metallic foam and zeolite with better thermal conductivity and higher heat transfer efficiency were developed to obtain shorter cycling time and thus a reduced reactor size per unit of power [26]. In Fujioka et al.'s study [27], composite reactants combining calcium chloride with expanded graphite and activated carbon fiber to promote the reaction between calcium chloride and methanol were investigated.

2.2.2. Selecting method for working pairs

Neveu and Castaiang [10], Orgaz and Dantzer [28] and Sun [29] have discussed some methods on the selection of chlorides and metal alloys. The followings discuss a thermal–chemical method using Clapeyron diagram to make the selection of chlorides for different types of heat transformers. The method is based on the Van't Hoff expressions of solid–gas reaction equilibrium and the liquid–vapor equilibrium as well as some matching relations. From the main purpose of heat transformers, the principle for selection is to realize maximum temperature lift under permitted temperature and pressure limits. Some hypotheses are made in order to simplify the selecting process: for a certain reactive salt $\Delta H_s = \Delta H_d$, $\Delta S_s = \Delta S_d$, and for the gas $\Delta H_e = \Delta H_c$, $\Delta S_e = \Delta S_c$. Having known the temperature of supplied middle-gradeheat, at first, real pressures are calculated by the following formula:

$$P = P[T_m - dT_1]_{eqL/G}, \tag{3}$$

or

$$P = P[T_m - dT_2]_{eqS/G}. \tag{4}$$

The calculated value should be within the pressure limits. And according to the cycles' Clapeyron diagrams, corresponding temperatures are derived from the following formula:

$$T = T[P]_{eqL/V} - dT_1, \tag{5}$$

or

$$T = T[P]_{eqS/G} - dT_2. \tag{6}$$

The suitable working pairs should also have the values within the temperature limits. Finally good temperature match and pressure match should also be met between different salts.

2.3. System performance

The quantity and quality of the middle-grade heat input are diverse, so performance evaluation is very necessary. The static performance parameters include COP, temperature lift, exergy efficiency, etc. Besides, various models are established to study the dynamic behavior of heat transformer systems, which is more useful for the establishment and improvement of practical systems.

2.3.1. Coefficient of performance and temperature lift

The two key parameters: coefficient of performance and temperature lift are defined as follows:

$$\mathrm{COP} = \frac{Q_\mathrm{h}}{Q_\mathrm{in}}, \tag{7}$$

$$\Delta T = T_\mathrm{h} - T_\mathrm{m}. \tag{8}$$

If the heat input is known, we can get the quantity of heat output from Eq. (7). And the temperature lift reflects the quality of heat output. Recently, another system efficiency called exergy efficiency has attracted more attention [30]. Exergy efficiency includes both quantity and quality of heat input and heat output, so it is considered more reasonable than conventional COP in characterizing system's efficiency. It is defined as

$$\mathrm{COP}_\mathrm{ex} = \frac{e_{x,\mathrm{h}}}{e_{x,\mathrm{in}}} = \frac{Q_\mathrm{h}(1 - T_0/T_\mathrm{h})}{Q_\mathrm{in}(1 - T_0/T_\mathrm{m})}. \tag{9}$$

The actual COP, exergy efficiency and temperature lift are more complicated, because different ratios of reactive gas to solid salt, various sensible-heat exchanges and unbalanced temperature differences should be taken into account [9]. The large heat capacity of the reactor vessels makes sensible heat recovery possible for pre-heating or pre-cooling to reduce the amount of heat input, and thus to obtain higher COP. Isselhorst and Groll have given out an expression of actual COP, in which sensible heat exchange efficiency ϕ_1 in the same reactor was introduced [20]. And if internal heat exchange efficiency is defined as ϕ_2, the actual COP and exergy efficiency of the two-stage four-salt cycle shown in Fig. 9 are

$$\mathrm{COP} = \frac{W_{\mathrm{G},4}\Delta H_{\mathrm{s},4} - (1-\phi_1)W_{\mathrm{S},4}C_{\mathrm{S},4}(T_\mathrm{h} - T_\mathrm{m})}{\sum_{i=1,3,4} W_{\mathrm{G},i}\Delta H_{\mathrm{d},i} + (1-\phi_1)[W_{\mathrm{S},1}C_{\mathrm{S},1}(T_\mathrm{m} - T_\mathrm{l}) - W_{\mathrm{S},3}C_{\mathrm{S},3}(T_\mathrm{h1} - T_\mathrm{m}) - W_{\mathrm{S},4}C_{\mathrm{S},4}(T_\mathrm{h} - T_\mathrm{m})]}, \tag{10}$$

$$\mathrm{COP}_\mathrm{ex} = \mathrm{COP} \cdot \frac{1 - T_0/T_\mathrm{h}}{1 - T_0/T_\mathrm{m}}. \tag{11}$$

The internal heat exchange process is described as

$$\begin{aligned} &\phi_2[W_{\mathrm{G},3}\Delta H_3 - (1-\phi_1)W_{\mathrm{S},3}C_{\mathrm{S},3}(T_\mathrm{h1} - T_\mathrm{m})] \\ &\quad = W_{\mathrm{G},2}\Delta H_2 + (1-\phi_1)W_{\mathrm{S},2}C_{\mathrm{S},2}(T_\mathrm{h1} - T_\mathrm{l}). \end{aligned} \tag{12}$$

The Van't Hoff expressions are as follows:

$$\ln P_1 = -\frac{\Delta H_2}{R(T_\mathrm{h1} - \mathrm{d}T_1 - \mathrm{d}T_2)} + \frac{\Delta S_2}{R} = -\frac{\Delta H_4}{R(T_\mathrm{h} + \mathrm{d}T_2)} + \frac{\Delta S_4}{R}, \tag{13}$$

$$\ln P_2 = -\frac{\Delta H_1}{R(T_\mathrm{m} - \mathrm{d}T_2)} + \frac{\Delta S_1}{R} = -\frac{\Delta H_3}{R(T_\mathrm{h1} + \mathrm{d}T_2)} + \frac{\Delta S_3}{R}, \tag{14}$$

$$\ln P_3 = -\frac{\Delta H_1}{R(T_\mathrm{l} + \mathrm{d}T_2)} + \frac{\Delta S_1}{R} = -\frac{\Delta H_3}{R(T_\mathrm{m} - \mathrm{d}T_2)} + \frac{\Delta S_3}{R}, \tag{15}$$

$$\ln P_4 = -\frac{\Delta H_2}{R(T_1 + \mathrm{d}T_2)} + \frac{\Delta S_2}{R} = -\frac{\Delta H_4}{R(T_\mathrm{m} - \mathrm{d}T_2)} + \frac{\Delta S_4}{R}. \quad (16)$$

So the actual temperature lift is derived as

$$\begin{aligned}\Delta T = {} & \Delta H_4/[\Delta H_4/(T_\mathrm{m} - \mathrm{d}T_2) + \Delta H_2/(T_{\mathrm{h}1} - \mathrm{d}T_2 - \mathrm{d}T_1) \\ & - \Delta H_2/(T_1 + \mathrm{d}T_2)] - \mathrm{d}T_2 - T_\mathrm{m},\end{aligned} \quad (17)$$

where $T_{\mathrm{h}1} = \Delta H_3/[(\Delta H_1 + \Delta H_3)/(T_\mathrm{m} - \mathrm{d}T_2) - \Delta H_1/(T_1 + \mathrm{d}T_2)] - \mathrm{d}T_2$.

Other cycles have the similar expressions.

2.3.2. *Comparison of chloride/ammonia heat transformers*

From the introduction of thermodynamic cycles, five kinds of cycles including the single-stage two-salt one, the two-stage three-salt one, the two-stage double-effect three-salt one, the two-stage three-salt one with internal heat exchange and the two-stage four-salt one with internal heat exchange are considered here for chloride/ammonia heat transformers. The selection of working pairs among 36 kinds of chlorides is shown in Fig. 10. Some operation parameters are given as follows: $P = 0.5-30$ bar, $T_1 = 15-40\,°\mathrm{C}$, $T_0 = 20\,°\mathrm{C}$, $\phi_1 = 0.5$, $\phi_2 = 0.7$, $\mathrm{d}T_1 = 5\,°\mathrm{C}$, $\mathrm{d}T_2 = 15\,°\mathrm{C}$ and

$$\Delta T \begin{cases} \geqslant 20\,°\mathrm{C}, & T_\mathrm{m} = 70\,°\mathrm{C}, \\ \geqslant 50\,°\mathrm{C}, & T_\mathrm{m} = 100\,°\mathrm{C}, \\ \geqslant 70\,°\mathrm{C}, & T_\mathrm{m} = 120\,°\mathrm{C}. \end{cases}$$

According to thermodynamic analysis, among the five kinds of chloride/ammonia heat transformers, only three kinds (the two-stage three-salt one, the two-stage three-salt one with internal heat exchange and the two-stage four-salt one with internal heat exchange) can meet the requirements for temperature lift, as shown in Fig. 13. The temperature lift of the single-stage system is lower, and that of the two-stage double-effect one is the lowest. The diagram also shows the maximum characteristics of the three two-stage systems. It is obvious that as the middle-grade heat temperature T_m increases, the COP, exergy efficiency, temperature lift, etc. are generally increasing.

For $T_\mathrm{m} = 70\,°\mathrm{C}$, when $20\,°\mathrm{C}$ or more temperature lift is required, only the two-stage three-salt system is feasible, and the COP and exergy efficiency are 0.35 and 0.48, respectively. When T_m reaches $100\,°\mathrm{C}$, the three-salt system and the two internal heat exchange systems are optional, and the former has relatively higher COP (0.37), higher temperature lift ($74\,°\mathrm{C}$), and thus larger exergy efficiency (0.59). As T_m increases to $120\,°\mathrm{C}$, the two internal heat exchange systems are feasible. Comparing with the four-salt system, the three-salt one has similar COP (0.3), but higher temperature lift ($127\,°\mathrm{C}$) and exergy efficiency (0.52).

From the calculation results of $T_\mathrm{m} = 100\,°\mathrm{C}$, the required coolant temperature T_1 of the two-stage three-salt internal heat exchange system is lowest, that of the four-salt internal heat exchange one is in the middle, and that of the three-salt one is highest. As for the high system pressure P_h, that of the four-salt system is higher than those of the other two. It is also noted that the double-effect three-salt system has a COP even higher than the single-stage one, but its temperature lift is too low for a heat transformer.

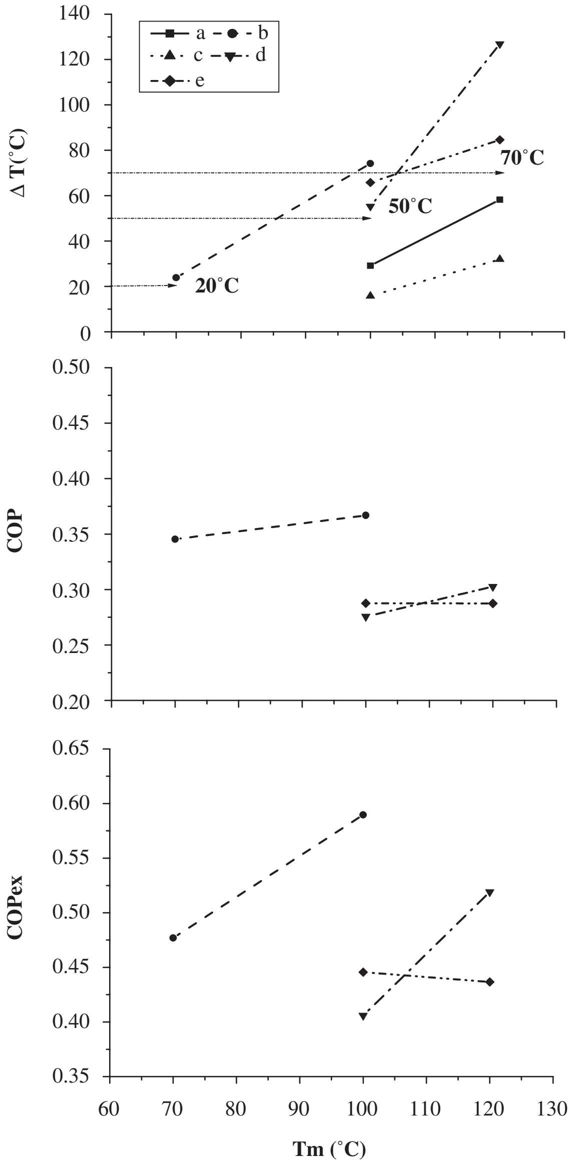


Fig. 13. Comparison of chloride/ammonia heat transformers. (a) Single-stage two-salt cycle. (b) Two-stage three-salt cycle. (c) Two-stage double-effect three-salt cycle. (d) Two-stage three-salt cycle with internal heat exchange. (e) Two-stage four-salt cycle with internal heat exchange.

2.3.3. *Models, simulation results and prototypes*

To optimize system design and operation, more details about the system should be known. Now many researchers are engaged in the model establishment to study conversion rate of reactive salts, transient power output, temperature, pressure change, etc. [31–35]. As the technology related to the heat exchanger is well established, the reactor that

concerns the complicated solid–gas reaction, heat and mass transfer becomes the most crucial component in the heat transformer system. Various models have been developed to simulate the dynamic behavior of the reactor.

Stitou and Crozat [36] classified these models into three kinds: local model, global model and analytical model. The local model is to establish partial differential equations concerning heat transfer, mass transfer and dynamic mechanics on infinitesimals and to solve them by numerical methods; the global model is to consider the reactor's characteristic variables and average parameters in some groups of differential equations; the analytical model is to use average parameters during the reaction process as variables, so the differential equations are only related to space variables. It can be seen that their differences lie in the method of how to deal with variables as well as the form of equations. Goetz et al. [37–39] have proposed grain-pellet model methods and shrinking-core model methods to solve these equations.

In the studies, the key factors are usually focused while some factors with less importance are ignored according to researchers' judgement. Stitou and Crozat [36] ignored mass transfer and used simple differential equations to calculate parameters of reactors. The linear relations of reactor's average power and its physical dimensions, working fluids, operation conditions were also given out. Lin et al. [40] established a general cyclic model, which was only affected by the irreversibility of mass transfer, and by using it, they calculated some important parameters like transient COP, rate of heat output, rate of entropy production, etc. Lu et al. [39] have formulated a general solid–gas reaction model coupled with mass transfer and chemical kinetics at the grain level and coupled with heat transfer at the pellet level. They also got a satisfactory correspondence to experimental results from this model.

Many researchers have applied these reactor models to the system simulation to get operational parameters or the effects of these parameters on system performance. Lebrun and Spinner [33] have used the general solid–gas reaction model in the calcium chloride/methylamine chemical heat pump system and obtained an approach for rapidly evaluating operational parameters for any suitable working pairs. Another model [41], which coupled chemical kinetics with energy conservation, was applied for the simulation of transient local temperatures, conversion rate of the reactive salt, etc. and good agreement was found between the simulation and experimental results. It could also be used to determine the influence of various parameters including kinetics, operation and configuration parameters of the reactive salt or of the reactor on system performance. Kang and Yabe [42] have done similar work by applying the cylindrical tube module to the thermal analysis of a metal hydride/hydrogen heat transformer and numerically investigating the effects of various design and operational parameters, such as cycling time, temperature of middle-grade heat source, heat transfer efficiency, etc. Their conclusions were consistent with Liang et al.'s analysis [43] that system efficiency can be improved by increasing temperature of heat source, enhancing heat transfer between reactors, reducing heat capacities of reactors and reactants, developing light-weight reactor vessels and recovering heat and mass between reactors.

Chen and Wu have done a lot of studies on heat transfer between external fluids and internal working media within the frame work of finite-time thermodynamics and gave out many useful methods for irreversibility reduction. They established the irreversible cycle model working between three heat reservoirs [44], the endoreversible cycle model working between four heat reservoirs [45] and the thermo-economic objective function [46] to get

optimized results much closer to real situation. These methods and results are quite valuable in optimal design and operation of real cycles. Still more work should be done to take the parameter of time into the analysis.

Based on above models, many researchers have given out the simulation results of heat transformer systems in their literatures. According to Goetz et al.'s analysis [5], the working pairs of chlorides/ammonia could realize high temperature up to 350 °C. Spoelstra et al. [47] calculated the large single-stage heat transformer system (power input of 5000 kW and power output of 2051 kW) with the working pairs of $MnSO_4$(6-2)/$NiCl_2$(6-2)/NH_3. When inputting heat at the temperature of 140 °C, cooling water at 30 °C, it could export heat as high as 239 °C, whose temperature lift reached 99 °C. Its maximum system pressure was 33 bar, COP and COP_{ex} were 0.41 and 0.618, respectively.

The simulation results help construct prototypes. On the other hand, the experimental results from prototypes can validate the model and offered some necessary parameters [39]. Bougard et al. [4] introduced a single-stage two-salt prototype with working pairs of $CaCl_2$(8-4)/$ZnCl_2$(4-2)NH_3, which upgraded middle-grade heat from 80–100 to 150–200 °C. It was reported that the measured system pressure was well fitted with the theoretical one. American ECI Institute [48] was reported to have developed a calcium chloride/methanol heat transformer with heat output temperature of 130 °C. Yanoma et al. [49] have designed and built a metal hydride/hydrogen heat transformer for commercial application and investigated parameters to find optimal operational conditions. Willers and Groll [50] presented an overview of experimental setup of a heat transformer prototype for industrial application, which provided continuous useful heat output of about 7 kW at the temperature of 190–200 °C with a driven heat of 130−135 °C and a cooling water temperature of 40 °C. Isselhorst and Groll [20] introduced a two-stage heat transformer prototype with three different metal hydrides, whose driven heat temperature was 130–140 °C, coolant temperature was 30–40 °C, and temperature of high-grade heat output was higher than 200 °C.

2.4. Application of heat transformers

Solid–gas heat transformers can be widely used in many fields. American BNL (Blackburn National Laboratory) has ever found that calcium chloride/methanol, magnesium chloride/water vapor, ammoniate/ammonia and metal hydride/hydrogen systems could be used in effective utilization of industrial waste heat and solar energy decades ago [51]; and it was reported that according to "Super heat pump, energy cumulation plan (1984)", Japan recovered waste heat which accounted for 50% of consumed energy [51]. Moreover, the high-grade heat from heat transformers can drive absorption and adsorption refrigeration or heat pump systems, so as to get better performance than those driven by the waste heat or solar energy directly; besides, when the temperature of high grade-heat is higher than 120 °C, it can be used to produce steam, and when higher than 230 °C, the steam can even drive the MP-steam grid to generate electricity [47]. Solid–gas heat transformer system can also store middle-grade heat easily in working pairs by decomposition reaction and release energy again when necessary by synthesis reaction to balance the time and space conflicts between heat supply and demand to improve energy use; and research [52] indicated that storing heat through reversible chemical reactions can be more effective and more reliable than conventional physical means: hydration/

Table 2
Products of metal hydride/hydrogen heat transformer [22]

Alloys	Working performance					Developer
	Temperature/°C			Cycling time (min)	COP/power (kW)	
	T_h	T_m	T_l			
$LaNi_5/LaNi_{4.7}Al_{0.3}$	90–100	60	20		3.5	Put into use; developed by American MPD Corp
$MmNi_{4.15}Fe_{0.85}/LaNi_5$	140–180	50–95	20–36		3.5	Developed by American Solar Trubines International
$LaNi_{4.9}Al_{0.1}/TiFe_{0.8}Ni_{0.2}$	58	42	15	3–6	50	Phototype; developed by Sweden Studvik Engergiteknik AB
$LaNi_{4.7}Al_{0.3}/LaNi_5$	90	65–75	15–25	6	0.38/3.5	Liquid–liquid heat exchanger; developed by two Japanese companies

dehydration reactions are most effective in low-grade or middle-grade heat storage; metal hydrides and ammoniates also have good performance. The principle of heat storage makes long-distance heat transport and district heat supply possible. The thermo-chemical long-distance heat transporting systems usually use working pairs of metal hydrides [53,54] (the working pairs of chlorides ammonia should also be feasible for the same working principle). And these thermo-chemical systems are proven to be better than conventional heated water systems especially for their low heat dissipation rate in the pipes. And the effective long-distance heat transporting system makes contributions to district heat supply between industrial, commercial and residential districts in the city planning in near future. Thanks to the friendly nature of working pairs to the environment, Choi and Mills [55] even investigated a heat transformer for upgrading waste heat in spacecraft theoretically.

Chloride/ammonia heat transformer system has advantages as various optional working pairs, simple and compact configuration, less requirement for temperature level of the driven heat reservoir, short cycling time, etc. So it is suitable for the use of solar energy or industrial waste heat. However, the disadvantages lie in problems caused by irritating smell, corrosion and high system pressure [16]. A lot of experimental research in solar energy storage and electricity generation has already been carried out [3], but still limited by complicated chemical kinetics, high requirement for safety, large investment, low system efficiency, etc., it has not been widely used yet.

Metal hydride/hydrogen heat transformer has merits as high density of heat storage and friendly nature to the environmental, etc., so it has a promising prospect in heat storage and solar energy utilization [52]. There are already many applications of the single-stage metal hydride/hydrogen heat transformer [22], as shown in Table 2. MPD Technology Corp in America developed a heat transformer of $LaNi_5/LaNi_{4.7}Al_{0.3}$ type alloys which is driven by middle-grade heat at 60 °C, cooled by cold source at 20 °C, and can export water or steam of 3.5 kW at 90–100 °C; two Japanese companies worked out the continuous $LaNi_{4.7}$ $Al_{0.3}/LaNi_5$ heat transformer system whose cycling time is 6 min, COP was 0.38 and temperature lift was 15–25 °C.

3. Areas of future research

Solid–gas reaction heat transformer is an effective application for energy saving: it is driven by industrial waste heat, solar energy, etc., and the working pairs are natural causing little damage to the environment. Although it is expected to have a promising prospect in the future, more efforts are needed today to solve many theoretical and practical problems such as complicated chemical kinetics, safety problem, low system efficiency, large investment, etc.

The chemical kinetics is crucial in the establishment of reactor models, but it still has many disputes. For example, one challenge comes from Aidoun and Ternan current research [56] on working pairs of $CoCl_2/NH_3$ in which they found the quasi-equilibrium equation between the synthesis and the decomposition reactions, which means such systems may be two-variable systems instead of single-variable ones. It is really a theoretical breakthrough to conventional knowledge and still needs more subsequent theoretical and experimental research.

The safety problem mainly comes from the high system pressure and the coexistence of liquid and gas in the same heat exchanger. Except for the improved manufacturing technology, choosing a proper thermodynamic cycle with suitable working pairs is indispensable. To ensure exactness of the expectation, more work should be done on the thermal properties of all kinds of working pairs.

The efficiency of solid–gas reaction heat transformers is limited a lot by the heat and mass transfer in the reactor. The poor heat conductivity of the solid salts and the porous structure are the main reasons for the bad heat transfer. The measures come from the mixed or composite salts with effective heat transfer and advanced structure of reactors. Moreover, searching for new types of multi-stage thermodynamic cycles, studying the effects of operational parameters, restraining the performance attenuation (expansion and agglomeration) of working pairs, etc. will also be helpful.

The improvement of system efficiency will increase the profits and thus reduce costs. Besides, developing the cogeneration of temperature lift, energy storage, long-distance heat transport, district heat supply, etc. will also help reduce total costs. Anyway, a scientific, reasonable and comprehensive economic analysis method should be established before the practical process.

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